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Title:

SOFT FOAMED LAYERED MATERIAL

Summary

The material according to the invention is defined as a substitute for natural leather in the shoe, clothing and furniture industry and possibly in other fields.

Its advantage is the fact that it can be prepared from aqueous dispersions of polymers, therefore without the use of organic solvents which in other procedures must be regenerated in large quantities which is economically unfavorable, and in which case it is impossible to prevent significant losses with respect to the effect on the environment (toxicity). Another advantage is the possibility of choosing a broad assortment of useful polymers.

The essence of the solution leading to the advantages described is the fact that the central layers are prepared by whipping an aqueous dispersion of a mixture based on polyurethanes, polyacrylates or rubber, possibly their mixture with a content of dry materials of 30-65 wt.% and adding surface active substances in a quantity of 0.01 to 5 wt. pt. per 100 wt. pt. of dispersion whose viscosity is modified by the addition of thickeners to 0.5-25 Pa·s.

Description

The invention concerns a soft inflated layered material composed of a covering polymer layer, a central porous polymer layer and a base textile layer which may,if desired, be impregnated with a polymer. The material is intended for use in the shoe and clothing and fancy goods industries and possibly elsewhere as a substitute for natural leather.

From the literature and on the market materials are known for the above noted applications, of which products based on polyvinylchloride predominate because of the low costs and polyurethanes because of the resulting physical-mechanical properties. Since good hygienic properties are required for application in the clothing and especially in the shoe industries, i.e. permeability and sorption of water, preference is given once more to the polyurethanes in the form of microporous layers prepared by a coagulation reaction.

The disadvantage of precipitation processes is the fact that it is necessary to regenerate the solvent in large quantities, which is unfavorable for the economics of the process. An especially serious shortcoming, however, is the fact that certain losses of toxic solvents cannot be prevented. For these reasons, efforts have been made to prepare porous without the use of solvents, e.g., from aqueous dispersions of polymers which eliminate the above-described shortcomings.

From the patent and company literature the use of aqueous dispersions of polymers is known for the production of layered flat materials both for the production of cover layers (homogeneous layers), the impregnation of the basic textile layers, adhesive (lamination) layers and also for the formation of the supporting intermediate layers, above all, porous layers.

The creation of porous layers in aqueous dispersions can be achieved by several techniques. For example, a layered material has been described from a central layer based on

polyurethane latex. The foaming of the central layer is caused by beating the mixture by driving air into it at a pressure of 0.6 MPa. The expansion occurs when the mixture is exposed to the free atmosphere. The shortcoming in this case is the need for special mixing equipment.

Another patent deals with the application of propellants in the latex. This method, however, is not suitable for the formation of high-quality porous structures and leads only to the formation of loose structures, because the inflating agent acts after the evaporation of water from the dispersions, therefore in the plastic state of the polymer.

In the case of a significant viscosity and limited deformability it is impossible to produce a high-quality porous structure. The addition of an inflation agent to the dispersion is therefore favorable only in the case of impregnation of the textile structure with a dispersion, since it increases the permeability of the impregnated structure.

A method has also been described for the production of foamed layers by beating nonionic polyurethane dispersions, application and drying. This method leads to the highest-quality structure formation by the solvent-free method, but it requires observance of relatively narrowly specified conditions. The content of the dry substance in the dispersion must be at least 45 wt.%, the viscosity of the mixture must be within the range of 0.2 and 1.2 Pa·s and the particle diameter in the dispersion must be no greater than 1 μm.

In this process, a dispersion without emulsifiers is used only with an addition of 0.1-10 vol.% of thickeners.

The purpose of the invention is to find a material which could be fabricated from a significantly broader assortment of types of ionogenic and nonionogenic dispersions based on polyurethanes, acrylates, rubbers, and polyvinylchloride. It was found that such a requirement is essentially satisfied by materials which can be obtained by beating an aqueous dispersion of a

mixture based on polyurethanes, polyacrylates or rubbers, possibly their mixture, with a dry substance content of 30-65 wt.% with the addition of a surface-active substance in a quantity of 0.01-5 wt.pt. per 100 wt.pt. of dispersion whose viscosity is modified by the addition of thickeners to 0.5-25 Pa·s, drying the layer of beaten foam and joining it to the basic covering layer.

An advantageous content of dry substance in the dispersion is greater than 45 wt.%. By adding a filler one increases the self-supporting capacity of the porous layer (the foam when dried is less inclined to collapse) and therefore one may also use a dispersion with a lower content of dry substance. The acceptable limit is up to 30 wt.% dry material with the possibility of the above noted thickening. The addition of thickeners to the dispersion cannot be defined suitably by the weight ratio, because each thickener has a different thickening capacity, nor by the achieved viscosity of the mixture.

A mixture with a viscosity lower than 0.5 Pa·s is very difficult to foam in such a way as to form a stable foam. A mixture with a viscosity higher than 25 Pas, however, after filling is difficult to apply by the usual methods and subsequently already requires such a large quantity of thickener which could negatively influence the properties of the porous layer.

The addition of surface-active substances such as ammonium stearate soap is necessary not only from the standpoint of forming a foam by whipping the dispersion (the addition promotes the achievement of a high quality time-stable foam) but also from the standpoint of the stability of the porous structure during drying and also from the standpoint of quality of the pores obtained. An addition of the surface-active substance of less than 0.01 wt.% per 100% of dispersion is not sufficient and the addition of more than 5 wt.% per 100% dispersion has an unfavorable effect above all on the hydrolytic stability of the porous film.

It was also found that in order to form the supporting intermediate layers of the laminated flat materials it is possible in many cases and also advantageous to use a filler for the dispersion. All of the currently known fillers are suitable such as ground chalk, ground or precipitated limestone, kaolin, bentonite etc. The addition of a filler can be utilized in every basic dispersion, but is only necessary in dispersions with a dry substance content less than 40 wt.% because of the above mentioned possibility of the collapse of the foam during drying. The addition of less than 0.01 wt. pt. of filler per 100 wt. pt. of dispersion does not influence the self-supporting quality of the porous layer, while the addition of more than 30 wt. pt. per 100 wt. pt. of dispersion leads to highly concentrated dispersions with poorer physical properties of the porous layer.

It was also found that the rheology of the foamed system based on an aqueous dispersions of polymers as well as the time stability of the wet foam, the stability of the foam when dried and the properties of the dried porous layer can be positively influenced by adding an accessory crosslinking agent, preferably a urea, phenol, possibly melamine formaldehyde condensate which may be partially etherified. The addition of less than 0.01 wt. pt. per 100 wt. pt. of dispersion has a negligible effect on the above listed parameters. The addition of more than 20 wt. pt. per 100 wt. pt. of dispersion limits the flexibility of the porous film to such an extent that the material is useless for the desired application.

The central supporting layers described can be combined with any covering layer (polyvinylchloride, polyurethanes, polyamides etc) and also with any base layer (woven fabric, knit fabric, nonwoven, impregnated textile material, fur. etc) depending on the method of subsequent use of the laminated flat material. The advantages of the finished material are the softness and the high vapor permeability caused by the intermediate supporting porous layer, because such a porous layer usually achieves low volume weight (100-300 kg/m^3), which in the

case of high quality porosity given by fine pores and flexibility given by the basic polymer are clearly the properties which have a decisive effect on the wearing comfort.

For a more clearly understandable explanation of the essence of the invention the following examples are given which, however, do not limit the scope of the invention in any way.

Example 1

A coating mixture was prepared which contained (in wt. pt.) the following components:

Aqueous dispersion of aliphatic polyurethane (50% dry substance)	100
Acrylate thickener	2
Ammonium salt of stearic acid (surface active substance)	1

By applying and drying the mixture a light central layer was prepared with a thickness of 0.15 mm and a volume weight of 300 kg/m^3. This layer was joined to the surface of a covering layer of thermoplastic polyurethane (area weight 20 g/m^2) with a polyamide surface modification (area weight 7 g/m^2). Then with an acrylate dispersion (0.07 mm) the attached nonwoven substrate layer was impregnated with butadiene-acrylonitrile rubber.

The produced material with a thickness of 1.2 mm has a permeability for water vapor of at least 1.5 $mg \cdot cm^{-2}h^{-1}$ and is suitable for footwear.

Example 2

A 0.15 mm foam layer with a volume weight of 400 kg/m^3 produced on a dried cover layer as in example 1 by whipping the following mixture (in wt. pt.)

Aqueous dispersion of polyurethane (40% dry substance)	100
Precipitated lime	20
Polyacrylate thickener	1.5
Phenolformaldehyde condensate	5
Pigment premix	2

Ammonium salt of stearic acid	4

After drying at 100-170°C on this layer a 0.1 mm acrylate lamination layer with the composition as in example 1 was applied.

For the lamination coating a fabric is applied, preferably cotton, possibly a cotton/polyester combination, rayon or polyamide with an area weight of 100-200 g/m^2. In the case when a lighter fabric is used, the lamination coating may be homogeneous, in the case of fabric with an area weight of ca. 200 g/m^2 it is preferable for the lamination coating to be applied in a volume weight of 400-600 g/m^3. It is advisable to use a fabric brushed in one direction and to apply in such a way that the brushed side forms the backing side of the product.

The material obtained is characterized by softness and good drape and is suitable above all for clothing.

Example 3

To a dried cover layer on a separation substrate obtained as in example 1 a 0.2 mm thick layer of foam were applied with a volume weight of 600 kg/m^3 produced by whipping the following mixture (in wt. pt.).

Aqueous dispersion of polyurethane (50% dry substance)	60
Aqueous dispersion of rubber (40% dry substance)	40
Floated chalk	10
Thickener (carboxymethylcellulose 5%)	5
Ammonium salt of stearic acid	1
Pigment premix	2

After drying of the layer the material was laminated with synthetic fur.

a) By lamination as in example 2 one combines the foam layer with a cotton woven with an area weight of 100 g/m^2. The material obtained is then laminated with artificial fur using a polyurethane foam by flame,

b) by direct lamination of the fur to the lamination coating of foam (layer thickness 0.25 mm) prepared according to example 1.

The material produced of type a) contains a textile intermediate layer which, however, has the advantage of complete prevention of the transfer of the nonuniformities from the backing side of the artificial fur to the face of the product.

Material of type b) is much simpler to produce, at the optimal thickness and quality of the porous layer it also has in a very high quality surface.

The two materials are suitable for clothing and shoes.

Example 4

On a separation substrate with a design a 0.1 mm layer of a 25% solution of thermoplastic polyurethane with an addition of 2 wt.% pigment paste is applied. After drying at 70-120°C on this layer 0.25 mm thick layer of foam is applied with a volume weight of 500 kg/m^3, which was obtained by foaming the following mixture on a high speed mixer (in wt. pt.):

Aqueous dispersion of aliphatic polyurethane (modulus 100%, 1.8 MPa, dry substance 40%)	70
Aqueous dispersion based on acrylate (dry substance 50%)	30
Finely ground kaolin	25
Polyacrylate thickener	1
Melamine formaldehyde condensate	
NH_4OH concentrated [pH] 8-9	3
Pigment premix	2
Surface-active substance	2

After drying at 100-170°C on this layer a 0.15 mm lamination layer of foam with a volume weight of 500 kg/m^3 is applied, obtained by whipping a mixture (in wt. pt.) of:

Aqueous dispersion of copolymer based on acrylate (dry substance 60%)	50
Aqueous dispersion of polyurethane (dry substance 40%)	50
Polyacrylate thickener	

NH_4OH concentrated pH 8-9 2

To the lamination coating a nonwoven fiber layer impregnated with microporous polyurethane is applied. After drying the lamination layer at 100-180°C the material is cooled and separated from the temporary substrate.

The layered material obtained has a thickness of 1 mm, a water vapor permeability minimally of 2 $mg \cdot cm^{-2}h^{-1}$ and is suitable for application for shoes.

Claims

1. Soft permeable layered material made up of a central porous polymer layer joined on the one side to a covering polymer layer and on the other side with a basic textile layer which may be impregnated with a polymer, in which case the central porous polymer layer is a product of drying of a layer of whipped foam and its joining to a substrate with a cover layer which is formed by whipping an aqueous dispersion of polymer, characterized by the fact that as the aqueous dispersion one uses a dispersion based on polyurethane, polacrylates or rubber, possibly their mixture with a dry substance content of 30-65 wt.% and with the addition of surface active substance in a quantity of 0.01-5 wt. pt. per 100 wt. pt. of dispersion, whose viscosity is adjusted by adding a thickener to 0.5-25 Pa·s.

2. Layered material as in claim 1 characterized by the fact that the whipped mixture for the central porous layer contains 0.01-30 wt. pt. of filler per 100 wt. pt. of polymer dispersion.

3. Layered material as in claim 1 characterized by the fact that the applied mixture for the central porous layer contains 0.01-20 wt. pt. of an accessory crosslinking agent per 10 wt. pt. of polymer dispersion.